Preliminary Survey - Characterization of Emissions from Ayerst Organics Ltd. Brandon, Manitoba

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Abstract

At the request of the Air Pollution Control Section of the Environmental Management Division, a survey was undertaken by operators of the Mobile Monitoring Unit to characterize emissions from Ayerst Organics Ltd., 720 17th Street East, Brandon, Manitoba.

Results from this study indicate that ammonia levels fall well below the maximum acceptable level of 2 ppm averaged over a one hour period. Sampling and monitoring for other constituents in the Ayerst plume indicated the presence of small amounts of hexanol, while other compounds were found to be below detectable limits.

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Background

Ayerst Organics Ltd., 720 17th Street East, Brandon, Manitoba, operates a plant for the extraction of certain conjugated estrogens from pregnant mares' urine. This material is the active ingredient in Premarin, a drug used in the treatment of certain post menopause disorders in women.

Plant process operations involve the use of solvent extraction to remove the required fractions from the urine. Solvents used include toluene, hexanol and ether. Storage facilities are provided for raw materials, extracted product and solvents. The product is then sent to another facility for further purification and drug manufacture.

At the request of the Air Pollution Control Section of the Environmental Management Division, a survey was undertaken by operators of the Mobile Monitoring Unit. Specific objectives of this study were:

1) To determine ambient ground level concentrations of ammonia which could be attributable to emissions from the Ayerst plant.
2) To characterize other constituents which may be emitted from the Ayerst plant.
3) To compare concentration levels to Manitoba Ambient Air Quality Objectives/Guidelines, where applicable ambient sampling was performed as meteorological conditions permitted, and as access to affected areas allowed.

Some emission testing was also undertaken at the source, to determine source concentrations.

In conjunction with other Brandon ammonia studies, previous monitoring was performed in the vicinity of Ayerst Organics [1]. Results of the last survey indicated that ambient ammonia levels were well below the Manitoba Ambient Air Quality Guideline value, based upon one hour time weighted average.

The following section summarize the applicable air quality objectives, sampling and monitoring procedures used, results and a discussion of data obtained.

2. Manitoba Air Quality Guidelines and Objectives

Manitoba Air Quality Guidelines and Objectives have been formulated for various air pollutants. Provincial criteria have been established for two levels:

Maximum Acceptable Level (MAL) - this level is intended to provide adequate protection against effects on soil, water, vegetation, materials, animals, visibility, personal comfort and well being.

Maximum Desirable Level (MDL) - This level defines long-term goals for air quality and provides a basis for anti degradation policy for the unpolluted parts of the province and for the continuing development of control technology.

2.1 Ammonia

Ammonia in an important compound for use in industry and agriculture, but is not considered a major environmental pollutant.

Continuous exposure to ambient levels (above 50 ppm) have been found to cause various disorders in plants and animals, while levels above 20 ppm have been found to cause irritation of nose and throat in humans.

The Manitoba Ambient Air Quality Guideline for Ammonia has set the maximum acceptable level at 2 ppm (1.4 mg/m^3) based upon a one hour TWA. This guideline is intended to protect people in residential areas from annoyance due to the odour of ammonia [2].

3. Procedures

3.1 AMMONIA

Monitoring for ammonia was performed using a TGM555 automated colourimetric analyzer with ammonia module installed. Ammonia present in the air sample is converted to ammonium ion in the presence of a dilute solution of sulphuric acid (0.1N). The ammonium ion in solution reacts with sodium salicylate solution in the presence of sodium hypochlorite to produce an intense, emerald green colour, which is measured by the colourimeter. The results were compared to a calibration curve prepared prior to the survey, to determine actual ammonia concentrations. This method is highly specific for ammonia, with few interferences.

3.2 Organics

Qualitative monitoring for hexanol and toluene was undertaken using a Foxboro model 128GC organic vapor analyzer, and a Photovac model 10A10 portable gas chromatograph.

The organic vapor analyzer (OVA) is a portable unit designed to measure either total hydrocarbons in ambient air, or specific compounds, using the gas chromatographic function. The detection principle is based upon flame ionization, in which a hydrogen flame is used to ionize contaminants present in the air sample. The constituents are detected at a collection electrode, which produces a current proportional to the number of ions or electrons present. The gas chromatograph function allows for separation of a mixture of components based upon their affinity for the column material used. For this study, a 24 inch 10% Supelcoport 60/80 mesh column was used.

The detection principle for the Photovac gas chromatograph is based upon photoionization. This process involves the absorption of ultraviolet light by a molecule, causing ionization to occur. Ionized contaminants are detected at a collection electrode, which generates a current proportional to the ion concentration present. An SE-30 column 4 feet by 1/8" diameter was used.

For both instruments, grab samples were taken of the ambient air using tedlar bags. The air samples were analyzed qualitatively in comparison to known reference standards.

3.3 Emission Monitoring

During the course of ambient monitoring in the vicinity of Ayerst Organics, periodic tests were undertaken using Gastec tubes for certain compounds (or classes of compounds). These were undertaken primarily as qualitative measurements to attempt to confirm the presence of certain suspected emissions. There is, however, the

possibility for some degree of quantitative measurement also as these same tubes are calibrated and graduated against known sources.

The tubes are glass packed, with specific indicating media and hermetically sealed. The tips are broken off both ends of tube (for use) and it is inserted into a pump. A specified number of pump strokes (100 ml/stroke) are performed in a recommended time period depending on the type of tube. The ambient concentration can then be either read directly or calculated from the scale etched on the exterior of the tube. The accuracy of the method is approximately ± 25%.

The tubes indicate the presence of specific compounds on the basis of colour change reactions. The following tubes were utilized one or more times;

1) Ammonia low range tube (No. 3L)

   Measurement Range - 1-60 ppm

   Detection Principle - Ammonia neutralizes sulphuric acid to change the colour of pH indicator (Cresol red)

   Interferences - Alkyl amines or hydrazine at a concentration of more than 1/10 that of ammonia adds a positive error.[3]

2) Amines tube (No. 180)

   Measurement Range - 1-180 ppm (depending on specific amine)

   Detection Principle - Amines neutraiize sulphuric acid change colour of pH indicator (Thymol blue). There is a wide variety of different amine, diamine and triamine compounds which will stimulate this reaction. With this tube it is not possible to distinguish individual amines when there is a mixture.[3]

3) Aromatic hydrocarbon/toluene tube (No. 122)

Measurement Range - <10-600 ppm

Detection Principle - Toluene reduces iodine pentoxide to liberate iodine, which produces a brown colour

Interferences - Various other hydrocarbons, organic vapours and carbon monoxide can contribute significant interference.(3)

4) Ethyl ether tube (No. 161)

Measurement Range - 0.04-1.0%

Detection Principle - Ethyl ether reduces potassium dichromate to form chromic sulphate.

Interferences - Various other organic vapours can cause interference.(3)

5) Ethyl alcohol tube (No. 112)

Measurement Range - 0.04-7.5%

Detection Principle - Ethyl alcohol reduces potassium dichromate to form chromic sulphate. This reaction is specific for alcohols (with no water present) and other organic vapours except alcohols do not react with the reagent.

Interferences - Some other alcohols yield positive results.(3)

Due to the interferences which are listed for the above tubes it was recognized that this sampling method does not lend itself well to the characterization study of unknown emissions, except in broad, generic terms.

3.4 Wind Speed and Direction

Wind speed and direction were obtained from an on board meteorological tower. A Windflo 540 wind speed and direction sensing instrument, manufactured by Athabasca Research Corporation Ltd., was mounted on the tower, which was raised to a 10 metre height. Wind speeds were recorded on strip charts during the monitoring program. The output from the anemometer is a voltage, and was converted to appropriate engineering units (i.e. km/hr). The same principle applied to the wind direction. Directions are given relative to true north taking into account the magnetic declination of approximately 5° east in the vicinity of Brandon.

4. Monitoring Sites

Monitoring was conducted at two sites during the course of the survey. All locations were less than 0.5 km from the Ayerst plant.

A site description of each location accompanies Map 1 in Appendix A.

5. Results

Hourly averaged concentrations for ammonia measured at each sampling site are shown in Table 1. Corresponding wind speed and directions measured are also included.

The sampling of the ambient air using Gastec tubes constitutes instantaneous grab sampling (over a few minutes), with the advantage of being able to read the results immediately. The following provisions apply to all tests conducted. Sampling was

always performed downwind of the point of emission and near the plume centre line (a subjective assessment based on odour intensity).

Table 1 - Ammonia Monitoring Results - Ayerst Organics

Date & Time	Site No.	NH_3 conc. (ppm) 1 hr. TWA	Wind Speed (km/hr)	Wind Direction (degrees)
April 9/85				
12:00-13:00	1	<0.1	31	200
13:00-14:00		<0.1	29	200
14:00-15:00		<0.1	32	220
15:00-16:00		<0.1	30	240
16:00-17:00		<0.1	33	240
17.00-18:00		<0.1	29	240
18:00-19:00		<0.1	25	280
19:00-20:00		<0.1	27	310
20:00-21:00		<0.1	24	300
21:00-22:00		<0.1	22	300
22:00-23:00		<0.1	29	300
23:00-24:00		<0.1	27	300
April 10/85				
00:00-1:00		<0.1	12	290
1:00-2:00		<0.1	14	280
2:00-3:00		<0.1	12	300
3:00-4:00		<0.1	12	290
4:00-5:00		<0.1	calm (<10)	315°
5:00-6:00		<0.1	14	310°
6:00-7:00		<0.1	calm (<10)	320°
7:00-8:00	2.	<0.1	calm (<10)	320°
8:00-9:00		<0.1	calm (<10)	320°
9:00-10:00		<0.1	calm (<10)	310°
10:00-11:00		<0.1	calm (<10)	310°

Table 2 - Survey Data Summary (a)

Site No.	Times and Date	No. of Hours	Average Conc. NH_3 (ppm)
1	12:00 9/4/85-7:00 10/4/85	19	<0.1
2	8:00 10/4/85-11:00 10/4/85	4	<0.1

Table 3 - Survey Data Summary (b)

	NH_3
Total No. of Monitoring Hours	23
Downwind Monitoring % of Total	10 43.5%
Average Concentration (ppm)	<0.1
Background (not downwind) Monitoring % of Total	13 56.5%
Average Concentration	<0.1

Gastec Tube Sampling Results

Test 1 - Toluene (tube No. 122) at 13:46 April 9, adjacent to monitoring site #1. Test consisted of 2 pump strokes (2 minutes/stroke). Results were negative, below detection limit which is 0.5 ppm.

Test 2 - Ethyl alcohol (tube No. 112) at 15:55 April 9, adjacent to monitoring site #1. Test consisted of 2 pump strokes (2 minutes/stroke). Results were negative. This test was to see if hexanol would be one of the alcohols which would also react in the tube. When the same tube was tested with an hexanol standard there was no response. Therefore, no further tests were conducted with the ethanol tubes. The same tube was then exposed to an ethanol standard and demonstrated a positive response.

On April 10, tests using Gastec tubes were taken on the roof of Ayerst directly at the main process vent and the storage tanks vent.

Results from Main Process vent:

1)	NH_3 (low range)	2 pump strokes	1 min/stroke	<2 ppm (trace)
2)	Amines	1 pump stroke	30 sec/stroke	<2 ppm (trace)
3)	Ethyl Ether	1 pump stroke	2 min/stroke	negative
4)	Toluene	2 pump strokes	2 min/stroke	negative

Results from Storage Tanks vent:

1)	NH_3	2 pump strokes	1 min/stroke	<2 ppm (trace)
2)	Amines	1 pump stroke	30 sec/stroke	<2 ppm (trace)

For ammonia, both emission tests were approximately equal at about 1 ppm. Thus, there didn't appear to be a difference in NH_3 emissions between the main process vent concentration and storage tanks vent concentration. For amines there was a marginally higher concentration from the main process vent.

Discussion

Monitoring was performed over a two day period April 9-10, 1985. Meteorological conditions were characterized the first day by brisk winds (25-35 km/hr) from a southerly direction, with cool temperatures, while light and variable wind conditions (less than 10 km/hr) with mild temperatures were experienced on day two.

The Ayerst plant normally operates from October to March or April of each year, with plant shutdown during the spring and summer. During this study, the manufacturing cycle was in normal operation, processing the final batch of urine for the season. Unprocessed urine is stored in large tanks prior to solvent extraction, with a chemical added as a preservative. These tanks were empty during the survey, and emissions from the tank vents could not be considered normal.

Site locations were chosen to provide access to the Ayerst plume, while precluding interference from other known sources of ammonia emission in the area. No exceedances of the Manitoba Ambient Air Quality Objectives for ammonia were recorded during this survey, with all values less than the detection limit of the instrument (0.1 ppm).

Throughout the survey, an odour could be detected in the vicinity of the MMU, when in a downwind venue from the plant. Ambient, qualitative monitoring was undertaken to try to characterize emission constituents in the Ayerst plume. Analysis using the organic vapor analyzer and Photovac chromatograph in comparison to known standards indicated the presence of small quantities of hexanol in the air samples taken, while the other constituents were at levels which were below the detection limit of the instruments. Hexanol has a sweet odour which can be detected at a lower odour threshold of 0.01 ppm[4]. No standards have been promulgated for this compound, and no limits have been set.

A downwind location from the plant was determined by comparison of wind direction and the compass bearing of the plant with respect to the monitoring site. This bearing, plus or minus 20° yields the direction range within which the receptor site is considered to be downwind of the source. This is only a generalization, however, and other factors, such as the distance from source to receptor, wind velocity and variability of the horizontal wind component will influence the range. For this study, the following ranges were used:

i) Site #1 is downwind of the Ayerst plant when the wind direction (hourly average) ranged between 200° and 240° (i.e. 220 $\pm$ 20°)

ii) Site #2 is downwind of the Ayerst plant when the wind direction (hourly average) ranged between 290° and 330°.

Emission monitoring was performed concurrently with the qualitative ambient monitoring. Tests utilizing various Gastec tubes at the main process and storage tank vents on the roof of the Ayerst plant indicated negligible emission quantities (see Results section). Further testing should be performed when the urine storage tanks are full to determine whether any elevation of emission levels for ammonia is observed.

Conclusions

Regarding the air quality measurements conducted during this study, it can be concluded that, under normal process operation, ambient ammonia concentrations in the vicinity of Ayerst Organics fall well below the maximum acceptable level as set out in the Manitoba Ambient Air Guidelines. Monitoring for constituents in the Ayerst plume indicated the presence of small amounts of hexanol, while other compounds were found to be below detectable limits.

References

(1) Szkolnicki, M. 1983. Brandon Ammonia Study No. 3: Ambient Ammonia Monitoring by the Mobile Monitoring Unit Air Standards and Studies Section, Environmental Management Division.

(2) Campbell, A. M. 1982 Proposed Ambient Air Guideline for Ammonia Department of Consumer and Corporate Affairs and Environment, Air Standards and Studies Section.

(3) Gas Precision Gas Detector System - Blue Book, 1982. Gastec Corporation, Tokyo, Japan.

(4) Journal Air Pollution Control Association 1974, Volume 24 p. 979.

Appendix

Appendix A:

Ambient Air Monitoring Sites

Site No. 1

Description: (a) North Side of Van Horne Avenue

(b) Approximately 100m West of 17th Street East

(c) Approximately 35m North of Ayerst plant

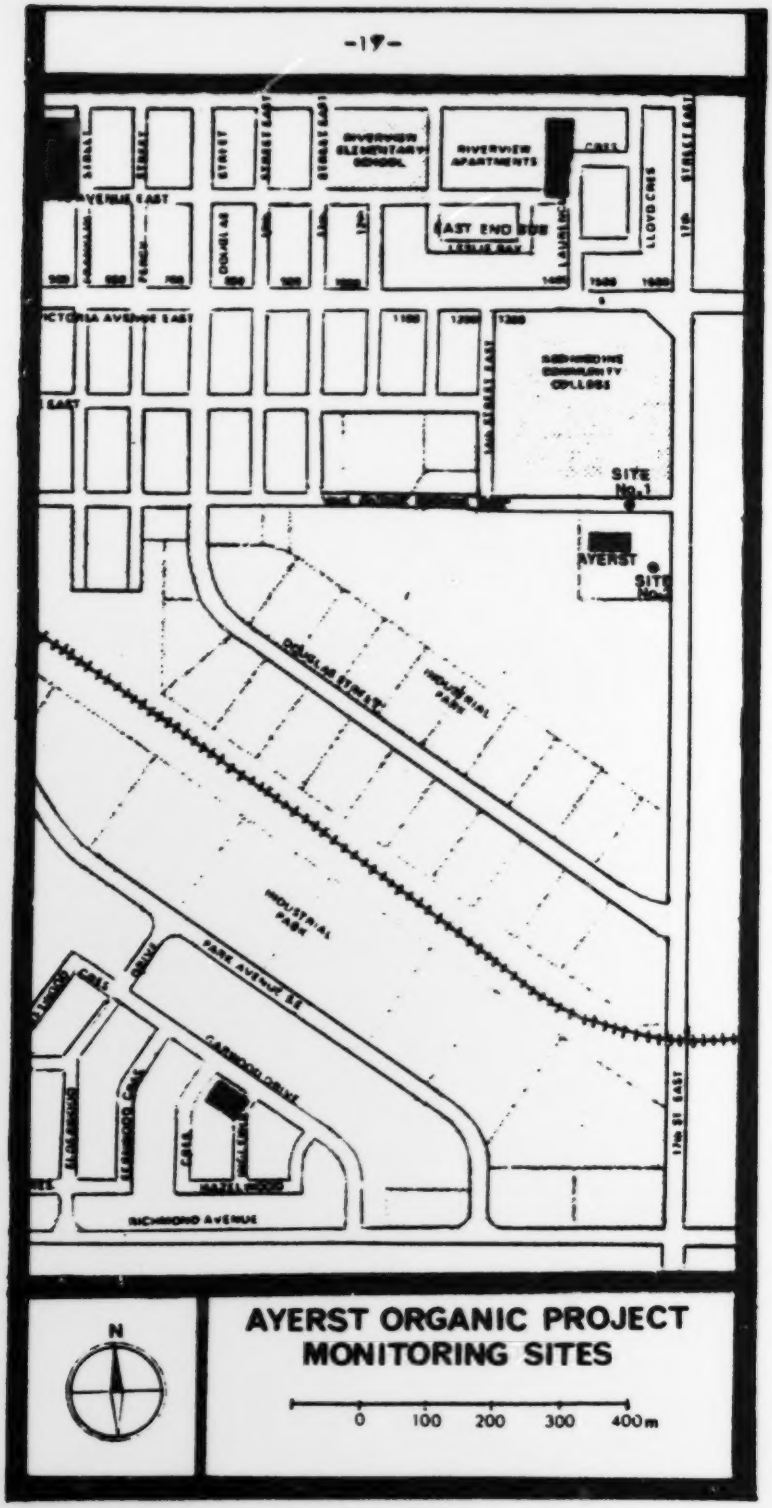
Site No. 2

Description: (a) Ayerst plant property, South East of plant

(b) Approximately 45m West of 17th Street East

(c) Approximately 150m South of Van Horne Avenue

(d) Approximately 50m South East of Ayerst plant


RIVERVIEW ELEMENTARY SCHOOL
RIVERVIEW APARTMENTS
EAST END BOWL
LLOYD CRES.
SITE No. 1
AYERST
SITE No. 2
DOUGLAS STREET
INDUSTRIAL PARK
INDUSTRIAL PARK
PARK AVENUE EAST
CARMOODY DRIVE
RICHMOND AVENUE
17th ST. EAST
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MONITORING SITES
0 100 200 300 400m